

Surface Chemistry and Catalysis

Definition(s) of Catalysis: Official IUPAC definition:

“a catalyst is a substance that increases the rate of reaction without modifying the overall Gibbs energy change in the reaction; the process is called catalysis...”

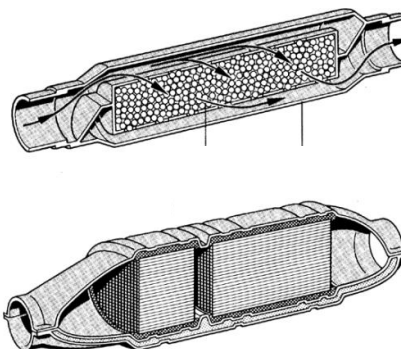
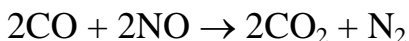
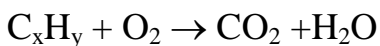
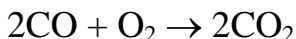
More commonly: *“a catalyst is a substance that increases the reaction rate without being consumed in the reaction”*

Importance of Catalysis

- Today approx. 90% of all industrial chemical processes can be related to catalysis
- Value of commodities produced via catalysis constitute typically 15-20% of the industrialized countries GNP
- Catalysts form the basis of a range of technological solutions to many urgent environmental - and energy issues. New challenges!

Example of Heterogeneous Catalysis: Automotive Catalysis

Engine exhaust contains significant concentrations of CO, NO_x and hydrocarbons (aromatics). In the three-way catalyst (**Pt/Rh** on CeO₂/BaO) the following reactions occur:



Ammonia synthesis: $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$

Catalyst: **Fe**, Ru

Steam Reforming Process for hydrogen production:



Fischer-Tropsch:

To produce hydrocarbons (gasoline) from coal.

First coal is partially burned to produce CO, which is then reacted with H_2 over **Fe, Co, Ni** based catalysts:



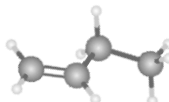
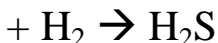
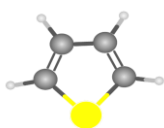
Hydrotreating Catalysis:

Hydrodesulfurization - (HDS)

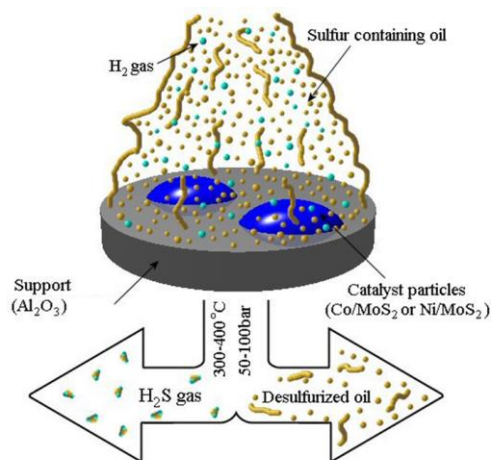
Hydrodenitrogenation - (HDN)

Hydrogenation - (HYD)

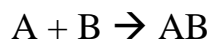
Catalyst: **MoS₂** (+Co)



+

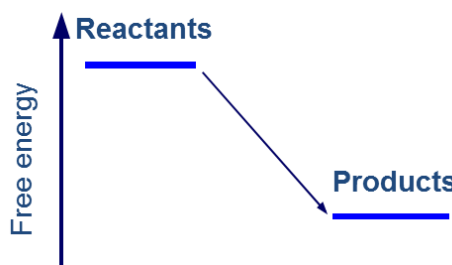


Molecular Reactions:



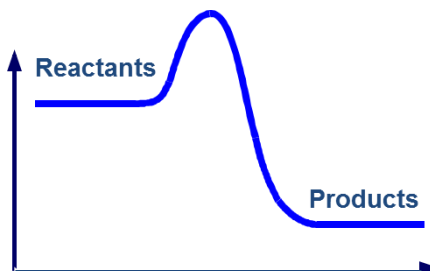
Thermodynamics:

- What is possible?
- Gibbs free energy



Kinetics:

-Energy barriers usually exist between reactants and products along the reaction coordinate. Therefore, even if thermodynamically possible not all reactions will proceed spontaneously



Adsorption of atoms and molecules on surfaces

We now discuss briefly the first step in a chemical reaction on the surfaces of any materials as a result of interaction with atoms and molecules.

Let's consider adsorption first.

Atoms and molecules bind to the surface by:

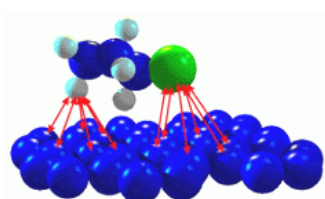
- weak van der Waals forces (physisorption)
- covalent chemical bonds
- ionic bonds.

In the first case the bonding energy is typically of the order of $\sim \text{meV}$.

In the second and third it is of the order of a $\sim 1 \text{ eV}$.

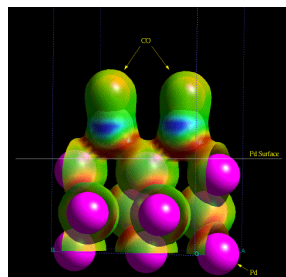
We immediately see that the relevant temperatures for physisorption are of the order of: $5 \text{ mV} = kT \rightarrow T \sim 50 \text{ K}$, and for chemisorption: $1 \text{ eV} = kT \rightarrow T \sim 2500 \text{ K}$

Physisorption:



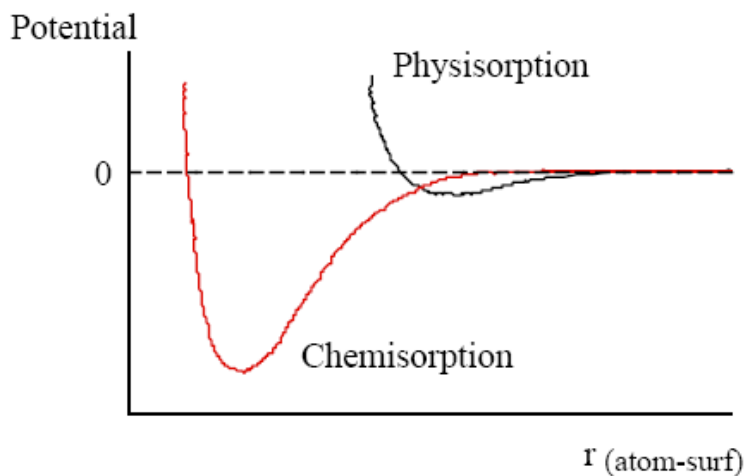
•Van der Waals forces

Chemisorption:



www.netsci.org/Science/Compchem/feature16.html

- Ionic bonding
- Covalent bonding
- Metallic bonding



Langmuir adsorption model

The rate of molecular collisions per unit surface area can be calculated from gas kinetic theory. For a pressure P and temperature T , this number is:

$$Z = P/(2\pi mkT)^{1/2}$$

Adsorption rate: $R_a \propto P \cdot k_a \cdot (1-\theta)^n$

k_a is the rate constant for adsorption $= v \cdot e^{-E_a/kT}$

Desorption rate: $R_d = -N_o \cdot d\theta/dt \propto k_d \cdot \theta^n$. where $k_d = v \cdot e^{-E_d/kT}$

The coverage at equilibrium is found by setting $R_d = R_a$, which leads to a relation:

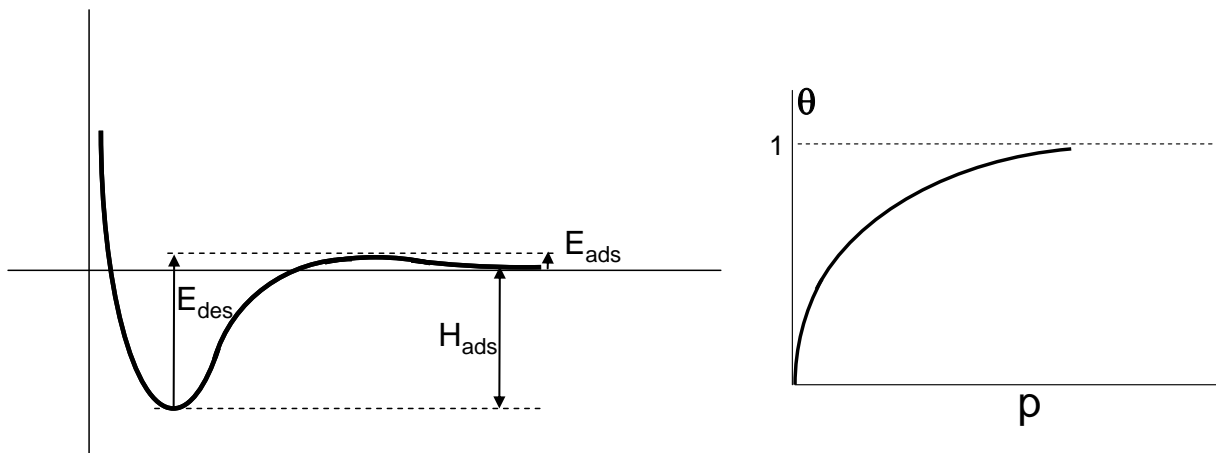
$$\theta = B \cdot p^{1/n} / (1 + B \cdot p^{1/n})$$

where $B = k_a / k_d = e^{(E_d - E_a)/kT}$.

This is the Langmuir isotherm. The basic assumptions of the model are that for a single adsorbate:

1. All sites are equivalent.
2. Each site can hold at most one molecule.
3. There are no interactions between adsorbate molecules on adjacent sites.

For molecular adsorption $n = 1$, for dissociative adsorption of a diatomic molecules $n = 2$



Thermal Desorption Spectroscopy

This is a powerful technique to study adsorption energies of atoms and molecules. One applies a linear temperature ramp to the sample: $T = T_o + bt$, typical heating rates are $b = 1$ to 10 K/sec.

This rate has to be set such that the pump in the system can effectively remove the gas so that no accumulation or pressure build-up occurs. The pressure is measured with a gas spectrometer sensitive to the mass of the desorbing product of interest.

$P = R_d/S$, where S is the pumping speed.

As the temperature increases the rate of desorption rate R_d increases exponentially. The pressure in the chamber is then proportional to R_d . The number of molecules ads. per unit area is $n = N_o.\theta$

$$P = R_d/S = -C.dn/dt = C.k_d.n^x = C.v.e^{-E_d/kT}.n^x$$

$x=1$ for first order, $x=2$ for second order

It is clear that as T increases k_d increases exponentially but n decreases due to desorption until all adsorbed molecules are desorbed.

First order processes:

Lets find the maximum temperature in the TDS:

$$0 = \frac{dP}{dT_m} = C.v. \frac{E_d}{kT_m^2} \cdot \exp\left(-\frac{E_d}{kT_m}\right) \cdot n + C.v. \exp\left(-\frac{E_d}{kT_m}\right) \cdot \frac{dn}{dT_m}$$

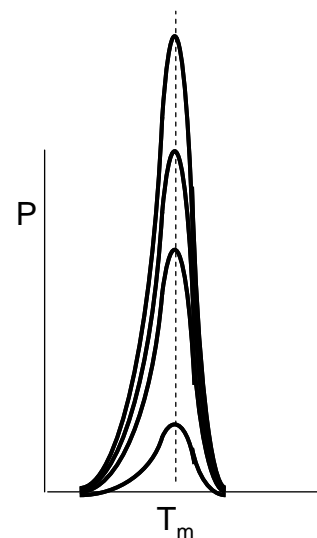
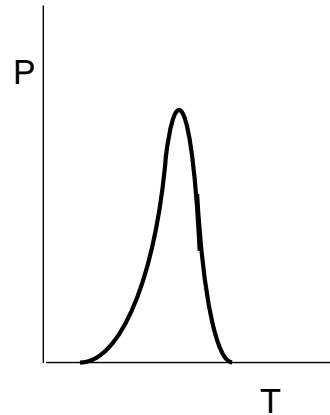
Since

$$v. \exp\left(-\frac{E_d}{kT_m}\right) \cdot n_m = -b. \frac{dn}{dT_m}$$

We get finally

$$b. \frac{E_d}{kT_m^2} = v. \exp\left(-\frac{E_d}{kT_m}\right) \rightarrow \text{the coverage } n_m \text{ does not}$$

enter here, so the maximum is independent of the coverage.



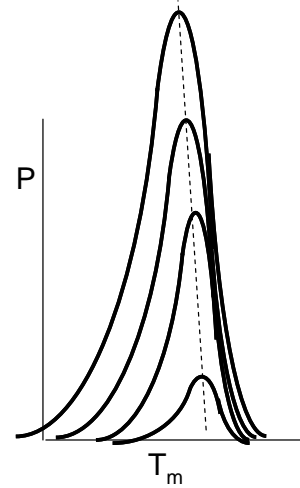
For a second order process:

$P = R_d/S = -C \cdot dn/dt = C \cdot k_d \cdot n^2$. Following the same procedure as before:

$$0 = \frac{dP}{dT_m} = C \cdot v \cdot \frac{E_d}{kT_m^2} \cdot \exp\left(-\frac{E_d}{kT_m}\right) \cdot n^2 + C \cdot v \cdot \exp\left(-\frac{E_d}{kT_m}\right) \cdot 2n \frac{dn}{dT_m}$$

This leads to: $b \cdot \frac{E_d}{kT_m^2} = 2 \cdot v \cdot \exp\left(-\frac{E_d}{kT_m}\right) \cdot n_m$

Now T_m does depend on the coverage n_m . The larger n_m the lower T_m . This is because the exponential grows much faster than the E_d/kT_m^2 term on the left. The TDS looks like the graph on the right.



Second order processes are typical for recombination reactions, such as $H + H \rightarrow H_2$ etc.

If we rewrite the formula above as: $\log\left(\frac{E_d}{kT_m}\right) = \log\left(\frac{2vn_m T_m}{b}\right) - \frac{E_d}{kT_m}$

Since $E/kT_m \gg \log(E/kT_m)$, in a first approximation a plot of $\log(n_m \cdot T_m)$ vs $1/T_m$ will be a straight line with slope E_d/k .

In a first order process v in k_d is roughly an infrared frequency $\approx kT/h = 10^{13} \text{ s}^{-1}$

In a second order process, v represents the frequency of collisions of the two atoms that recombine. The order of magnitude therefore is:

$4r \cdot v \cdot n = k_d \cdot n^2$, where r is the radius of the atom and v its surface thermal velocity. Using $\frac{1}{2}mv^2 = kT$ we get $v \approx 4r(2kT/m)^{1/2} \approx 10^{-2} - 10^{-3} \text{ s}^{-1}$

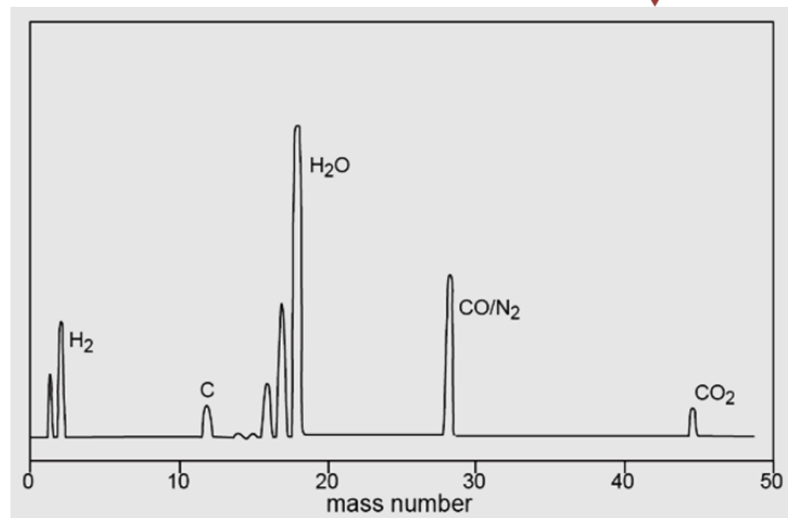
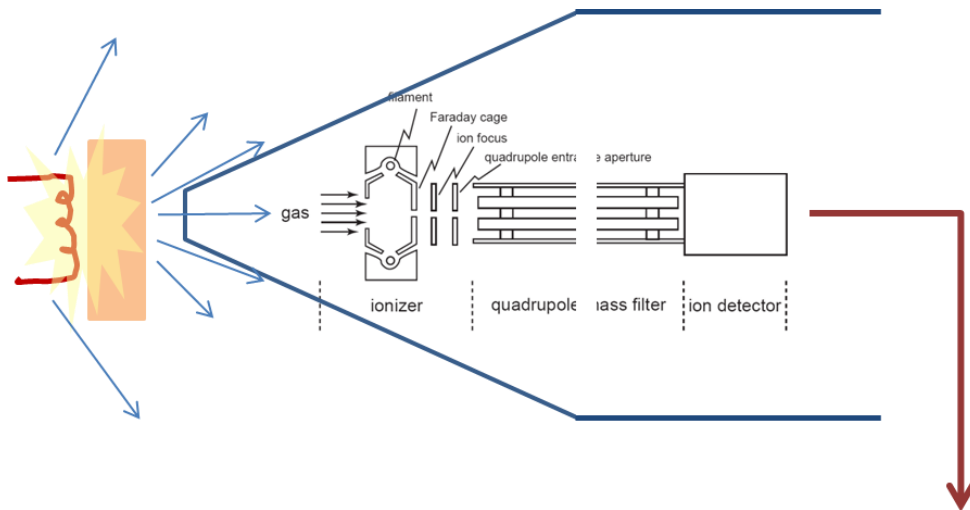
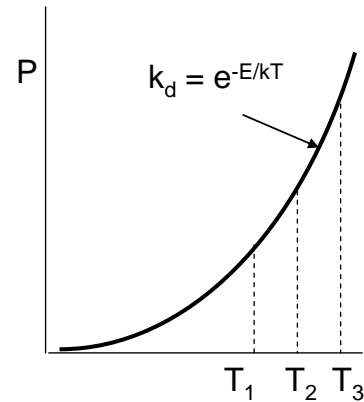
Zeroth order processes

These are processes where the desorption rate does not depend on the coverage. For example lines of atoms where the end atoms desorb only. The lines shrink with time as T increases but as long as there is a line (albeit shorter and shorter) the rate is the same. Another example is the evaporation of multilayers. As long as the first layer is not reached the desorption remains constant.

$P = R_d/S = -C \cdot dn/dt = C \cdot k_d \cdot n_o$, where n_o is the density of centers (e.g. lines of atoms)

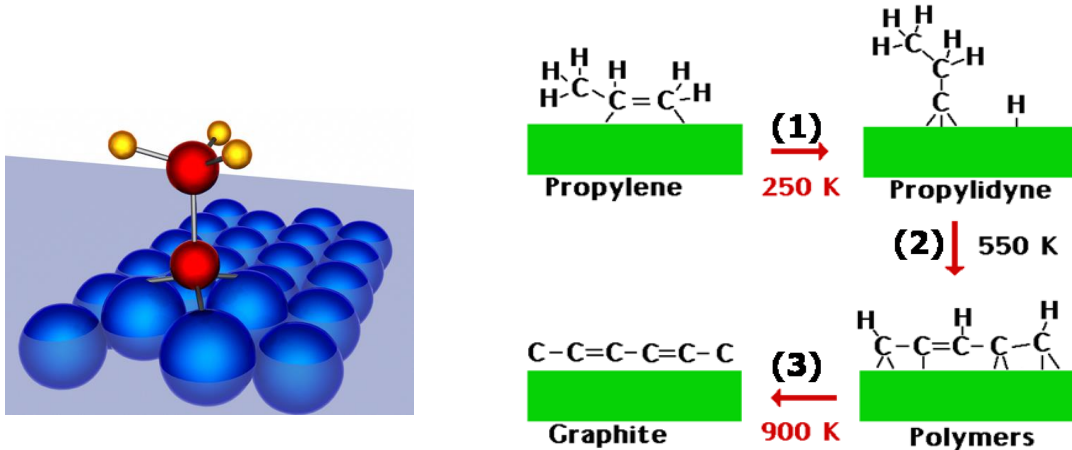
In that case P grows as k_d until the coverage goes to zero, where it then drops to zero.

Example of experimental set-up using a mass spectrometer encapsulated so that the ionizer captures only gases desorbing from the sample:



Examples:

1. One example of the use of TDS is to study reactions, for example the dehydrogenation of alkanes:



This is how the thermal desorption spectrum looks like for the dissociation product H_2 :

